Rapid Determination of Total Sulfur in Fuels Using Gas Chromatography with Atomic Emission Detection

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Abstract

The purpose of this study is to determine whether gas chromatography (GC)–atomic emission detection (AED) can be used in a low-resolution mode for rapid, accurate determinations of total sulfur in fuels at trace levels to complement other popular methods of total sulfur analysis. A method for the rapid determination of total sulfur in fuels (called "fast GC–AED") is developed. The method is tested on gasoline, jet fuel, kerosene, and diesel fuel with sulfur concentrations ranging from 125 mg/L down to 2.5 mg/L. Fast GC–AED shows better performance than traditional GC–AED for total sulfur determinations, especially for complex mixtures containing many different sulfur-containing compounds at trace levels. This method also shows that GC–AED can be used for both rapid determinations of total sulfur and traditional determinations of speciated sulfur without requiring equipment changes. Fast GC–AED is competitive with other popular methods for sulfur analysis. The 5-min program that is developed for fast GC–AED is comparable with the time scale of other methods, such as wavelength dispersive X-ray fluorescence and UV-fluorescence (2 to 5 min). Fast GC–AED also compares favorably with UV-fluorescence for trace sulfur determinations, demonstrating accuracy down to 2.5-mg/L sulfur.

Introduction

Because of environmental concerns, regulatory agencies are continuing to force a reduction of sulfur levels permitted in transportation fuels. These new regulations will require those who manufacture, transport, and store fuel to accurately determine trace levels of sulfur in order to ensure compliance and prevent contamination. Information about total sulfur content will also be needed to evaluate the emission characteristics of fuel mate-

rials and make decisions about the blending of feedstocks. The most popular methods that are currently used for performing total sulfur determinations include energy dispersive X-ray fluorescence (EDXRF), wavelength dispersive X-ray fluorescence (WDXRF), UV-fluorescence (1), and sulfur chemiluminescence detection (SCD) (2). In addition, gas chromatography (GC) coupled with an atomic emission detector (AED) is popular for the separation and quantitation of individual sulfur compounds because of its element-selective response, and also because of its low limit of detection and structure-independent elemental response (3–9). However, the typical analysis times associated with GC–AED discourage its use for routine total sulfur determinations. Typically, total sulfur determinations in petroleum products using GC–AED involve a partial separation of the sulfur components in the sample, followed either by integration of the net response on the sulfur channel (emission at 181 nm) (10) or by integration of individual peaks and the summation of their concentrations to attain a total sulfur number (5). One drawback to using GC–AED for the quantitative speciated sulfur analysis of petrochemical samples is that the length of time required to obtain an adequate separation of the components of interest is on the order of 30 to 50 min per sample. Other ASTM methods used for the quantitative analysis of sulfur, such as ASTM D 4294 (EDXRF), ASTM D 2622 (WDXRF), and ASTM D 5453 (UV-fluorescence), require only several minutes per sample. Other drawbacks to quantitative GC–AED are related to the quantitation method itself. Use of the net response of the sulfur channel involves arbitrary choices of the optimum baseline, while use of the peak-summing method can yield a low biased result because sulfur components present at these trace levels produce peaks that are not distinguished from the background but still should be included when calculating the total amount of sulfur present in the sample.

This study describes a method for determining trace levels of sulfur in fuels using GC–AED with minimal separation of the individual sulfur components. The method, ("fast GC-AED"), employs a combination of a rapid temperature ramp with elevated carrier gas flow rates to minimize the degree of separation of the sulfur compounds in the sample. The method results in a more compact chromatogram containing the total sulfur response, thus minimizing the subjectivity in selecting a baseline for integration and removing some of the bias from the sulfur determination. This method of minimal separation chromatography could be broadly applicable to other sulfur-selective detection systems, such as SCD. Although similar methods have been proposed employing a short, deactivated column with other sulfur-specific detectors (11), fast GC–AED requires no column changes to perform both rapid total sulfur determinations and speciated sulfur analysis. The goals of this work were to determine whether the accuracy and low detection limit of the fast GC–AED technique can compete with other ASTM methods in terms of time required, accuracy, and precision, and to determine whether in certain cases fast GC–AED demonstrates better performance than traditional GC–AED for total sulfur determinations. The fast GC–AED method that has been developed for analyzing trace levels of sulfur in fuels has been tested on jet fuels, gasoline, and diesel-range materials and has been validated using appropriate reference materials. Advantages, disadvantages, and limitations of the fast GC–AED method are also described. With GC–AED, it is possible to perform both total sulfur analysis and speciated sulfur analysis using the same experimental setup simply by varying the chromatographic conditions.

Experimental

The GC–AED system used for this work was a 6890 GC (Agilent Technologies, Wilmington, DE) coupled to a 2350A AED (Joint Analytical Systems, Ludlow, KY). The system was equipped with an autosampler (ALS 7683, Agilent Technologies) to perform all of the injections. ChemStation software (Version B.02.05, Agilent Technologies) was used to perform data acquisition and processing.

Fuel samples used for this study included gasoline, jet fuel, and diesel fuel. The samples contained a wide variety of sulfur concentrations ranging from 150 mg/L to below 15 mg/L. Also, a standard reference fuel (NIST SRM 1616a, Sulfur in Kerosene, National Institute for Standards and Technology, Gaithersburg, MD) was used for the analysis of the raw fuel and in a diluted form to evaluate performance at low sulfur concentrations. An additional fuel matrix (a sulfur-free kerosene sample) was used for the dilution of more concentrated samples and for spike recovery studies to evaluate method performance at low levels.

Calibration was performed by two different external calibration methods. One method involved the injection of di-n-butylsulfide in iso-octane at three different concentrations. The other method involved a multicomponent mixture of sulfur compounds in iso-octane. The mixture was comprised of di-n-butylsulfide, benzylphenyl sulfide, and diphenyl sulfide, each at different concentrations. Using this method, calibration was performed with a single injection.

In order to determine an optimum set of chromatographic conditions, a series of runs was performed on a typical jet fuel sample. The parameters that were optimized included inlet pressure, injection volume, split ratio, and temperature program. Table I shows the parameters that are used for the typical speciated analysis of sulfur in fuels by GC–AED (12,13). The table also shows the optimized set of parameters that were used as the final nonseparation parameters for the fast GC–AED method, as discussed in subsequent sections of this study. The column used was chosen because it is a popular choice for speciated sulfur determinations by GC–AED, and one goal of this study was to show application of the fast method using the same column as used for speciated analysis. Detector parameters remained similar to recommended settings for traditional sulfur analysis.

Results and Discussion

Shown in Figure 1 is a sulfur chromatogram using a "standard" jet fuel analysis method and a sulfur chromatogram using the final optimized chromatographic parameters for fast GC–AED. As shown in Figure 1B, the total elution time for the entire suite of sulfur compounds was on the order of 5 min. This is a dramatic time savings compared with the typical times required for traditional total sulfur analysis (as illustrated in Figure 1A), which range from 30 to 60 min for complex mixtures or heavier fuel fractions. Figure 1 shows that it is possible to obtain all of the information about sulfur content in the same amount of time in which traditional GC–AED shows baseline for the sulfur channel.

The final optimized program represents a tradeoff between speed and detector capabilities. Although the AED is highly selective for sulfur, at extremely high carbon-to-sulfur ratios, carbon emissions interfere with the sulfur emission lines used by the 2350A detector. If the entire unseparated sample reached the

Table I. Experimental Parameters for Traditional and Fast GC–AED

Column	Rtx-1701 (Restek) (14% cyanopropylphenyl, 86% dimethylpolysiloxane); 30-m × 0.32-mm i.d., 1-μm film thickness	
Detector	Sulfur emission	181 nm
	Reagent gases	Oxygen (65 psi)
		Hydrogen (55 psi)
	Make-up flow	Nitrogen (100 mL/min)
	Transfer line temperature	300°C
	Cavity temperature	300°C
	Traditional GC–AED	**Fast GC–AED**
Inlet	280°C, 12 psi (constant)	280°C, 20 psi (constant)
Injection	1.0 μL (neat), 50:1 split ratio	0.5 μL (neat), 20:1 split ratio
Oven	40°C to 300°C at 10°C/min, hold at 300°C for 10 min	190°C for 0.5 min, 190°C to 280°C at 25°C/min

detector, the sulfur information would be lost in the emission interference from the hydrocarbon components in the fuel matrix. Therefore, a minimal amount of separation is necessary to allow a portion of the hydrocarbon matrix to pass through the detector prior to the sulfur elution. ChemStation software can be used to perform data-processing algorithms to minimize the effects of coeluting hydrocarbons. A factor known as "back amount" is used to suppress the contribution of background emission to the sulfur chromatogram. It must be stated that this back amount factor plays a significant role in determining whether peaks that appear in the sulfur chromatogram are resulting from sulfur compound emission or carbon–oxygen molecular emission. Allowing a minimal degree of separation also helps to prevent overloading of the detector, protect the delicate plasma discharge tube, and minimize deleterious effects on downstream components, such as the lenses and optics system of the spectrometer.

In traditional GC–AED determinations of total sulfur in fuels, a partial separation of the fuel is performed and the sulfur emission is monitored to acquire a chromatogram. Integration of the chromatogram is done in one of two ways. One method involves the integration of individual peaks, with the total sulfur concentration being determined by summing the contributions of the individual peaks. Although this method may be accurate for less complex chromatograms, it lends itself to a negative bias for cases
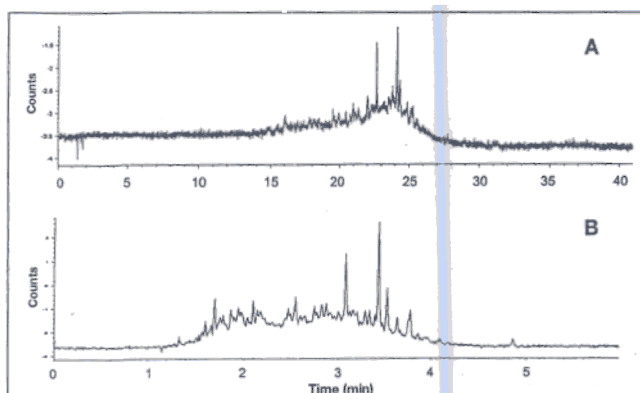
in which minor peaks may not be integrated because they are near the baseline, thus yielding a low result. The other integration method involves a manual integration of the entire area of the sulfur-specific chromatogram. This method involves an arbitrary selection of the starting point of the sulfur signal, with a "best fit" line being drawn to incorporate the response from start to finish. This method is susceptible to negative bias because trace peaks may be interpreted as noise by the operator and would therefore be excluded from the integration. In addition, this method may be less accurate because the arbitrary choice of baseline position may vary significantly from sample to sample or even for the integration of the same chromatogram by different analysts.

These integration biases are illustrated in Figure 2, for the analysis of a diesel fuel. Figure 2A shows the sulfur-specific chromatogram for a traditional GC–AED analysis. The first integration (shown in the figure as the solid line with start and end points extended up from the chromatogram), from an arbitrary starting point, yielded an area of 490. The second integration (shown in the figure as the dashed line with start and end points extended below the chromatogram), by another analyst who chose a different starting point, yielded an area of 570 units. The integration areas determined by the two analysts for the same chromatogram resulted in a difference of 15.5% in calculated concentration. However, using fast GC–AED (shown in Figure 2B) results in a more concise chromatogram in which the begin-

Figure 1. Comparison of sulfur-specific chromatograms for the analysis of a jet fuel using (A) traditional GC–AED and (B) fast GC–AED.
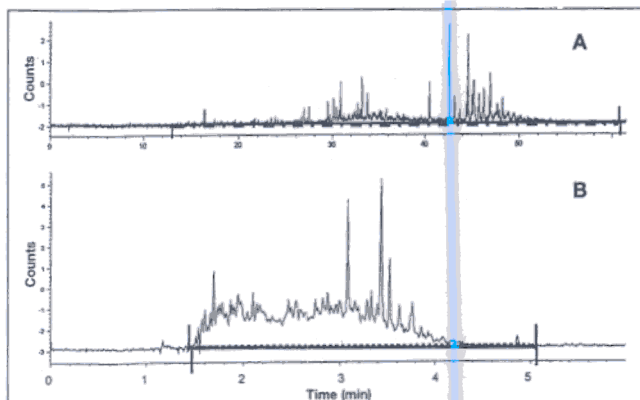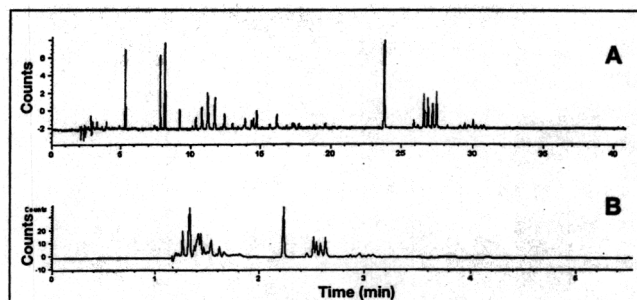

Figure 2. Integration differences for the same chromatogram using (A) traditional GC–AED and (B) fast GC–AED for the analysis of sulfur in a diesel fuel sample.

Figure 3. Comparison of the ability of (A) traditional GC–AED and (B) fast GC–AED to provide accurate analysis of a complex mixture of trace sulfur compounds in a gasoline sample.

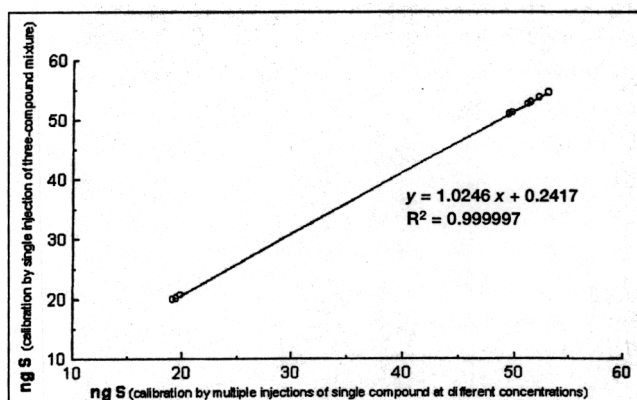$$y = 1.0246 x + 0.2417$$
$$R^2 = 0.999997$$

Figure 4. Calculated concentration of sulfur using different calibration methods, which were calibrated using multiple injections of a single compound versus single injection of a mixture of three compounds, each with different concentrations.

ning of the sulfur response is indicated by a more dramatic rise in response. Thus, the subjectivity involved in choosing the baseline for the sulfur response is minimized. In this particular example, the integration areas measured for the two operators were different by a mere 10 units, and the resulting concentration determinations varied by only 4%. This example illustrates the potential variation that is inherent in quantitative sulfur analysis by traditional GC–AED and the ability of fast GC–AED to minimize that variation.

In a traditional GC–AED chromatogram, the spreading of the individual sulfur components may make it difficult to distinguish trace components from the baseline. This results in a low bias for the calculated sulfur concentration using typical GC–AED. For fast GC–AED, in which the components are not given the opportunity to separate, a concentrated solute zone containing the entire suite of sulfur-containing compounds reaches the plasma. A rapid rise in baseline is achieved because the trace components are incorporated into a concise region of sulfur response. This makes the fast method more accurate for determining total sulfur concentration, especially for samples composed of many different sulfur compounds at low concentrations. This improvement in total sulfur determination using fast GC–AED is shown in Figure 3 for a gasoline sample. Traditional analysis, with integration of the total sulfur signal, yielded a sulfur concentration of 107 mg/L sulfur. Fast GC–AED analysis, which integrates the total response in a more compact region of the sulfur chromatogram, yielded a sulfur concentration of 126 mg/L sulfur. Independent analysis by UV-fluorescence determined the concentration to be 122 mg/L sulfur, indicating that fast GC–AED was more capable of incorporating all sulfur compounds into the net sulfur response, compared with the traditional method, which did not include the contribution of many trace sulfur components. The bias between methods would not necessarily depend on the level of sulfur, but would depend on the number of trace sulfur-containing components in the sample. These trace components, if allowed to separate, would be more difficult to differentiate from the baseline noise.

One feature of the AED that makes it possible to perform total sulfur determinations of complex mixtures is its linear, structure-independent response. If the detector response was not independent of the structure and type of sulfur compound, accurate quantitation of total sulfur (which is composed of many different structural components in fuel materials) would be impossible. Therefore, this fast method is uniquely applicable to detectors that demonstrate structure-independent response. Although the method should be appropriate for SCD (11), the rapid elution of unresolved sample components may lead to quenching problems with the pulsed-flame photometric detector (13,14). A response factor for sulfur can be generated using a single sulfur-containing standard, which can then be used to quantitate all sulfur compounds in the matrix. External calibration involves the injection of one sulfur compound at different concentrations. Thus, multiple injections are required to perform the external calibration. In this study, a calibration mixture was created using three different sulfur compounds, each with different concentrations. Because these compounds are separated from one another prior to reaching the detector, the detector responds to each compound individually. In this way, a 3-point calibration can be performed in a single injection, further reducing the analysis time typically associated with the more traditional method for quantitative analysis. Additional calibration components can be used, provided that adequate separation is achieved during the analysis program. Figure 4 compares the experimental results for total sulfur determination for several samples using both calibration methods. The figure shows that calibration using multiple injections of a single compound and a single injection of a multiple-component sample yields the same results. However, if a small bias is introduced when a single calibration compound is used, using a calibration solution that contains different structures may minimize this bias by incorporating the response of the instrument to a variety of different sulfur-containing compound structures into the calibration.

In order to evaluate the accuracy of the fast GC–AED method for determinations of sulfur at low levels, a wide variety of fuel materials were analyzed. These fuels were also analyzed by at least one other independent method of sulfur analysis. Table II provides a comparison of the results. The study shows that accurate determinations are possible at concentrations ranging from approximately 125 mg/L through trace sulfur concentrations of 5.5 and 2.5 mg/L. Also, the analysis time for each sample is competitive with other preferred methods for total sulfur analysis, which typically require 3 to 5 min per sample.

A second goal of this work was to determine how fast GC–AED

Table II. Comparison of Fast GC–AED and Independent Analysis for Trace Levels of Sulfur in Fuels

Sample	Fast GC–AED*	Independent Result
Commercial gasoline	133.5 ± 20.2	122 (120,123)†
SRM 1616a (sulfur in kerosene)	111.3 ± 5.2	111.2 ± 1.4‡
ASTM gasoline sample	51.6 ± 7.8	52 (52,52)†
Diluted SRM 1616a	5.40 ± 0.6	5.5§
Spiked sulfur-free kerosene	2.75 ± 0.25	2.5**

* Results presented as concentration of sulfur in milligrams per liter ± 95% confidence interval (n = 3).
† Average result for two measurements of the same sample by UV-fluorescence, with individual results in parenthesis.
‡ Result from NIST Certificate of Analysis, concentration of sulfur in milligrams per liter ± 95% confidence interval.
§ Calculated concentration based on certified concentration and 1:20 dilution factor.
** Calculated concentration based on reference compound concentration.
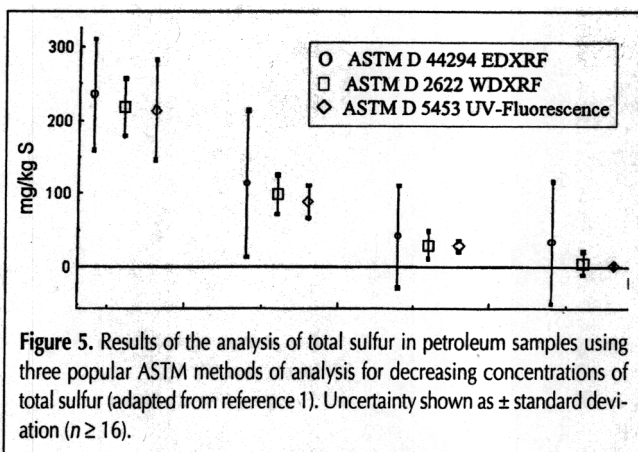

Figure 5. Results of the analysis of total sulfur in petroleum samples using three popular ASTM methods of analysis for decreasing concentrations of total sulfur (adapted from reference 1). Uncertainty shown as ± standard deviation (n ≥ 16).

compares with other popular methods of analysis for sulfur in petroleum samples. Figure 5, adapted from reference 1, shows the results of the analysis of total sulfur in petroleum at different sulfur levels using three popular ASTM methods. As the figure shows, the performance of the EDXRF method was poorer as the concentration of sulfur decreased, while the uncertainty of the WDXRF method expanded at low sulfur levels. Only one method, UV-fluorescence, performed adequately at levels of 5 ppm and lower. In terms of analysis time, the fast GC–AED method, which has demonstrated sample analysis time on the order of 5 min, can compete with these popular methods. In terms of accuracy and precision at low levels, the fast GC–AED method has been used in this study to accurately determine sulfur concentrations down to 2.5 mg/L, which surpasses the detection limits of the EDXRF method, improves the uncertainty of the WDXRF method, and is competitive with the UV-fluorescence method.

Although the fast GC–AED method has demonstrated good performance for trace sulfur determinations in gasoline, kerosene, and jet fuel samples, use of this method is likely limited to similar low-to-moderate boiling fuel fractions. Neat injections and minimized separations may not be appropriate for heavier fractions (such as crudes) because these more viscous sample types may have detrimental effects on the GC inlet system and increase the difficulty of obtaining a rapid elution prior to detection. Other potential limitations may be encountered because of the more delicate components of the AED detection system, including the discharge tube and optics system. These remain to be evaluated for the long term use of the method. For the short term, no problems were experienced with regards to discharge tube integrity or instrument response at low sulfur levels in light petroleum-derived liquids. Overall instrumental performance did not appear to degrade over the several months of testing of this method.

Conclusion

By varying appropriate chromatographic parameters, GC–AED can be used in a "minimal separation" mode for total sulfur determinations. Fast GC–AED has demonstrated good performance for low-level sulfur determinations compared with traditional sulfur analysis by GC–AED. Using fast GC–AED reduces analysis times, minimizes integration differences, and yields more accurate results, especially for complex mixtures that contain many different sulfur-containing compounds at trace levels. This "minimal separation" mode for total sulfur determination is also applicable to other sulfur-specific detection systems, provided that the detector response is linear and structure-independent and that the detector is capable of withstanding a relatively large solute zone containing the sample.

Fast GC–AED is competitive with other popular methods for sulfur analysis. In terms of analysis times, the 5-min program of fast GC–AED is comparable with the time scale of other methods, such as WDXRF and UV-fluorescence (2 to 5 min). In terms of the accuracy of the determinations, fast GC–AED is competitive with UV-fluorescence as among the most accurate analytical techniques at low milligrams-per-liter levels of sulfur.

The research in this study demonstrates that GC–AED can be used for both rapid determinations of total sulfur and traditional determinations of speciated sulfur. By adjusting the chromatographic parameters, information can be obtained about the total amount of sulfur in the fuel samples, as well as the compound classes that contribute to the overall sulfur content.

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